

PNNL Subsurface Scientific Focus Area Starting October 2008

Role of Microenvironments and Transition Zones in Subsurface Reactive Contaminant Transport

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PNNL SFA Science Team

Principal Investigators (2)

- ▶ **John Zachara and Jim Fredrickson**

Co-Principal Investigators (9)

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External Collaborators (12)

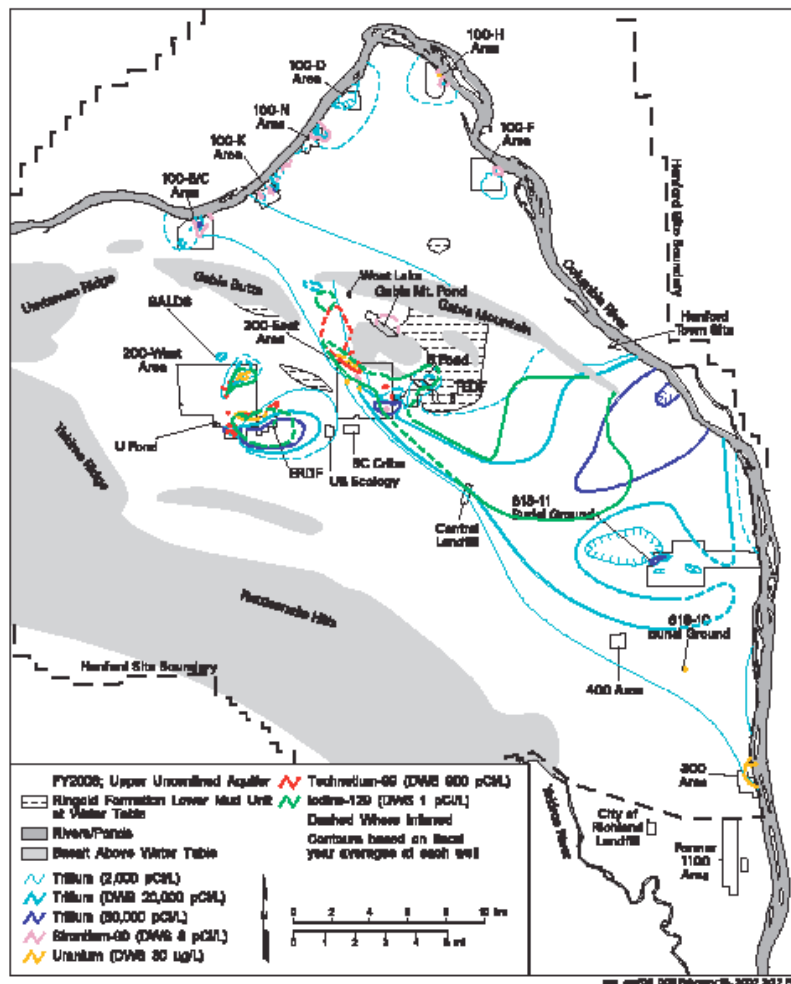
- ▶ **Steve Conradson (LANL), James Davis (USGS), Scott Fendorf (Stanford), Ken Kemner (ANL), Rob Knight (U CO), Frank Löffler (GA Tech), Melanie Mayes (ORNL), David Richardson (U of E Anglia), Eric Roden (U WI-Madison), Daad Saffarini (U WI-Milwaukee), Roelof Versteeg (INL), Brian Wood (OR State)**

**geochemistry, microbiology, hydrology, geophysics, spectroscopy,
biochemistry, molecular and multi-scale modeling**

Concept

- ▶ **Hanford-inspired subsurface science theme**
- ▶ **Hanford Site has long-term concerns and science issues (over 40 publications by PNNL staff with acknowledged Hanford Site impact)**
- ▶ **Close alignment with Hanford 300 Area Integrated Field Challenge, utilization and leveraging of EMSL and other DOE capabilities**
- ▶ **Seamless projects integrated across different scales around common hypotheses**
- ▶ **Research sufficiently fundamental for broad application to DOE and other contaminated sites**

Hanford Site – DOE's Largest Legacy Waste Site



- ▶ > 1000 contaminated “soil sites” [cribs, retention basins, disposal trenches, solid waste burial grounds]

Pu , ^{137}Cs , ^{90}Sr , U , ^{99}Tc

- ▶ 177 massive storage tanks with 53 million gallons of HLW and LLW. 67 suspected leakers

^{137}Cs , ^{90}Sr , U , ^{99}Tc , Cr

- ▶ Over 15 well developed groundwater plumes

U , Cr , ^{99}Tc , ^{129}I , ^{90}Sr , NO_3 , CT

- 200 Area plateau

- Columbia River Corridor

- ▶ 4 major canyon complexes

- U plant, B plant, REDOX, PUREX

Contaminant Emphasis

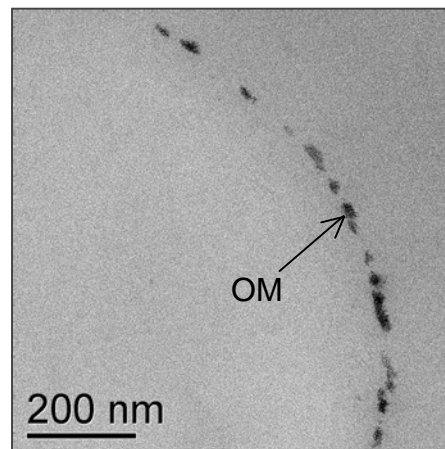
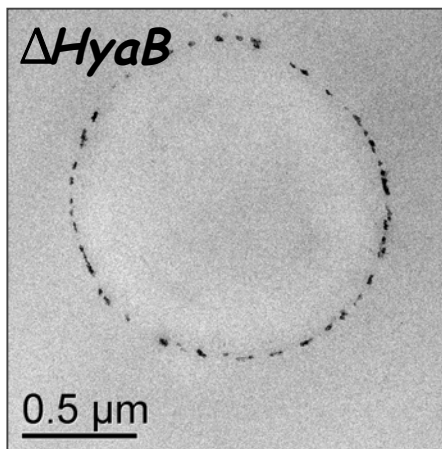
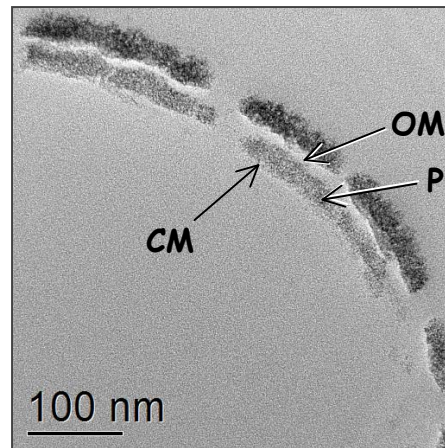
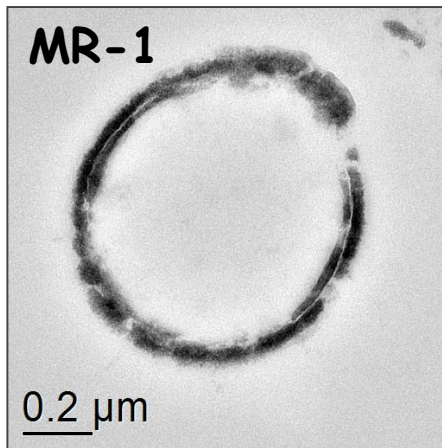
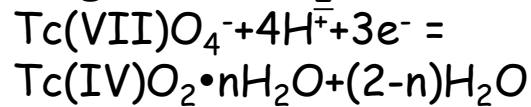
- ▶ Risk drivers on the Hanford site:
 - U, ^{99}Tc , ^{129}I , Cr, and CCl_4 – environmental mobility and persistence
 - $^{239,240,241}\text{Pu}$, ^{137}Cs , and ^{90}Sr – lower mobility but high radioactive toxicity
- ▶ PNNL's SFA focused on U, ^{99}Tc , and Pu
 - Polyvalency with complex biogeochemistry
 - Significant inventory
 - U = 202,703 kg, ^{99}Tc at 1390 Ci, and Pu at 400 kg
 - Long term concerns and scientific issues
 - Important science opportunities

Research Opportunities at Hanford

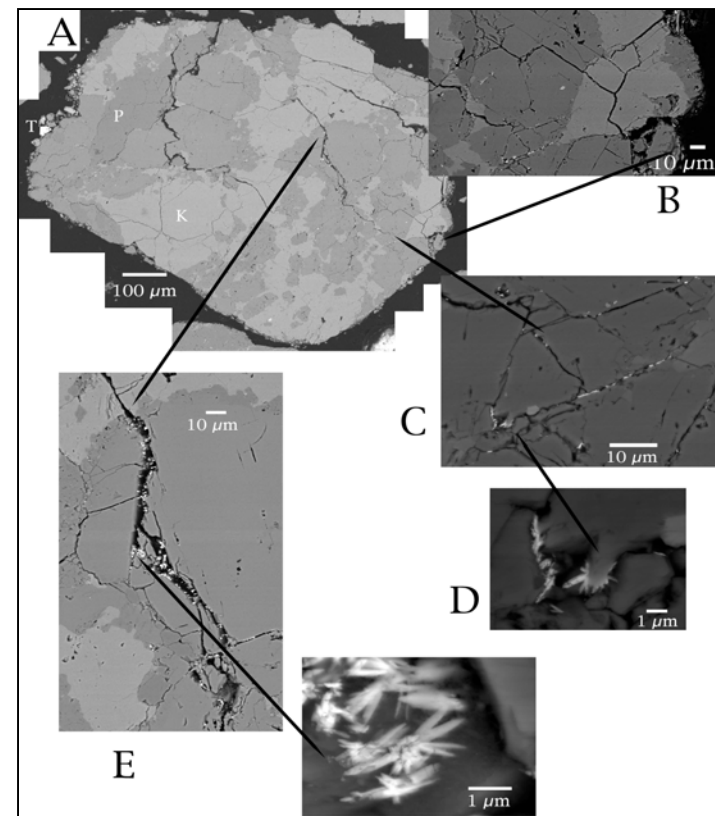
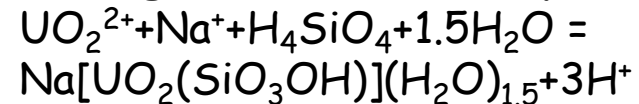
- ▶ **Environmental radiobiogeochemistry**
- ▶ **Intermediate duration environmental kinetics (25+y)**
- ▶ **Redox chemistry at various scales mediated by ferrous minerals**
- ▶ **Deep vadose zone processes**
- ▶ **Reactive transport at different scales**
- ▶ **Microbiology and biogeochemistry of linked groundwater-river systems**
- ▶ **Diverse subsurface microbial habitats – vadose, capillary fringe, aquifer, hyporheic etc.**

Microenvironments – Disproportionate Influence on Chemistry

Biogenic TcO_2



Intragrain U(VI) Precipitates

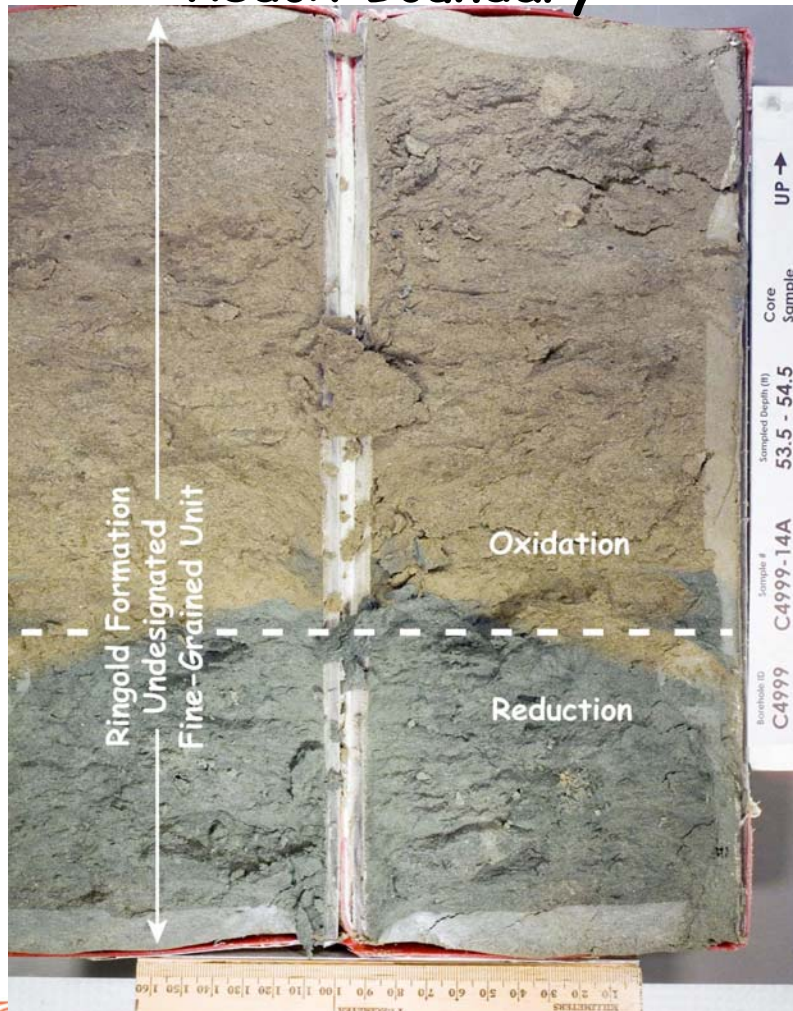


(McKinley et al. 2006, *GCA*)

Pacific Northwest National Laboratory
U.S. Department of Energy

Transition Zones – Exhibit Chem-Phys-Bio Changes Over Short Distances

Ringold Formation
Redox Boundary



Columbia River
Hyporheic Zone



(Moser et al. 2003, *ES&T*)

Different Scales ~ Different Issues

SFA

IFC

Molecular

- Bonding environment and local structure
- Fundamental mechanisms
- Energetics and structural controls
- Solvation effects

Microscopic

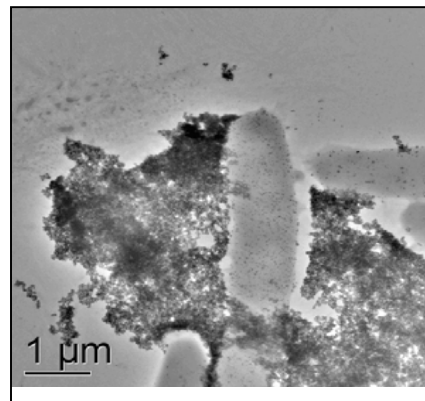
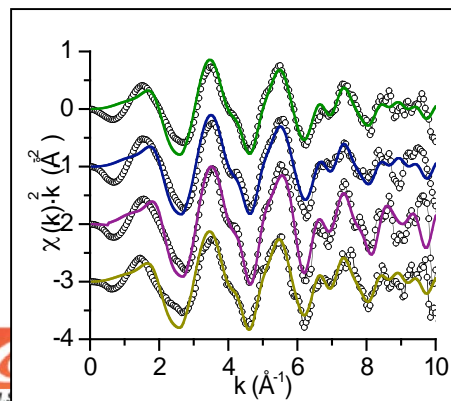
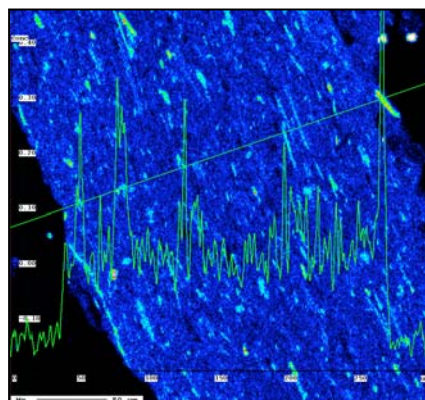
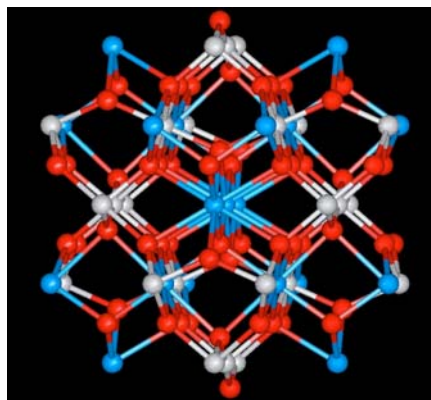
- Mineral residence phase identity & composition
- Reaction networks and kinetics
- Morphologic and surface issues
- Fundamental process coupling

Macroscopic

- Rate processes
 - Chemical
 - Microbiologic
 - Mass transfer
- Advection effects
- 1-D scaling issues
- Pore scale process coupling

Field

- Physical heterogeneity
 - Water velocities/directions
 - Reactants
- Multi-scale mass transfer
- Mixing & averaging
- Distributed properties
- Seasonal issues (temperature, precipitation)



SFA/IFC Relationship

- ▶ **IFC Theme: Multiscale mass transfer controls on reactive transport**
 - Field research with site-specific emphasis
 - Provides context for significance of microenvironments and transition zones
 - Field-scale reactive transport modeling
- ▶ **SFA Theme: Role of microenvironments and transition zones in reactive transport**
 - Laboratory and limited field research with fundamental emphasis
 - Microenvironments and transition zones give rise to mass transfer effects important to field-scale transport
 - Pore-scale reactive transport modeling with upscaling to define field-scale models and parameters

SFA and IFC efforts are fully complementary across multiple scales

Hanford IFC Field Research

(Geophysical, geological, and geostatistical characterization - SFA and IFC)

Facies-scale geometry

Pore-scale characterization

Pore-scale simulations

Upscaled models and parameters

- Lab-scale reactive transport validation
- Utilized in field-scale model of IFC

Guiding Hypotheses

- ▶ **Microbial community structure & function determined by local microscale conditions and mass transfer properties of sediments.**
- ▶ **Microenvironments & transition zones will be dominant regions of contaminant reaction.**
- ▶ **Diffusion-controlled mass transfer will establish & maintain microenvironments.**
- ▶ **Dominant processes within such domains will vary with scale (microns to meters).**

Microbiologic & Geochemical Characterization of Deep Borehole Sediments

Summer 2008 -- ~20 samples across geological formations and transition zones joint w/ IFC

Cultivation-independent analyses

► Biomass

- Direct microscopic counts
- Phospholipid phosphate
- % Respiring cells

► Phylogenetic / functional diversity and relative abundance

- Census of Bacterial/Archaeal 16S rRNA gene sequences (JGI CSP Sanger sequencing + pyrosequencing)
- Real time PCR for specific phylogenetic and functional groups

► Assessment of potential for U or Tc reduction

- Amend samples with electron donor
- Depend upon natural abundance of Fe(III) or exogenously added ferrihydrite as terminal electron acceptor (TEA)

Cultivation-dependent analyses

- Enrichment cultures with various TEA's
- High-efficiency cultivation strategies
- Analysis of metabolic versatility in cultivars

Provide Hanford-relevant microbes for molecular- to pore-scale research

Multivariate statistical analysis of microbial census + geochemical / mineralogical data to generate hypotheses for field-scale studies

A wide-angle photograph of a large, calm body of water, likely a lake or a wide river, under a clear blue sky. The water is a deep blue color, reflecting the sky. In the distance, a line of trees and some low hills are visible on the horizon. The foreground is dominated by dry, brownish vegetation, including tall grasses and shrubs, suggesting an autumn or late summer setting. The overall scene is peaceful and scenic.



Office of Science
U.S. DEPARTMENT OF ENERGY

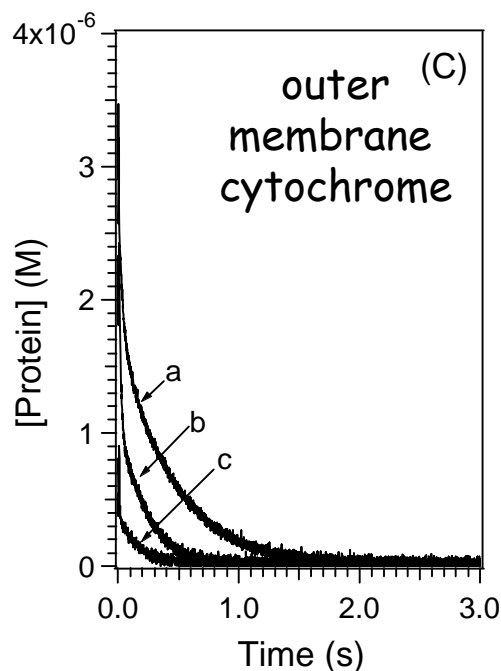
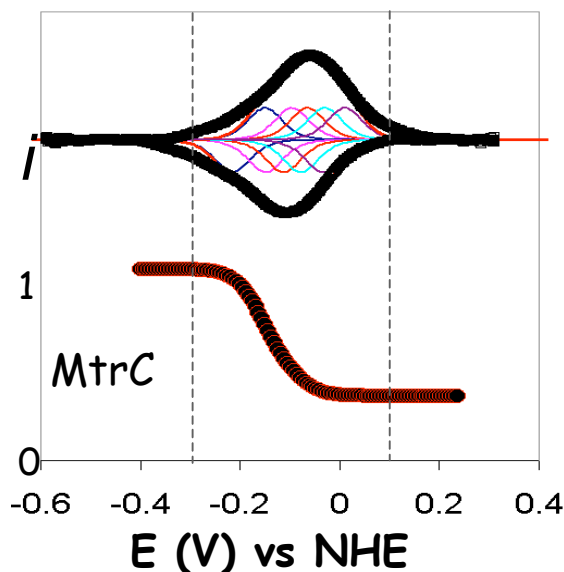
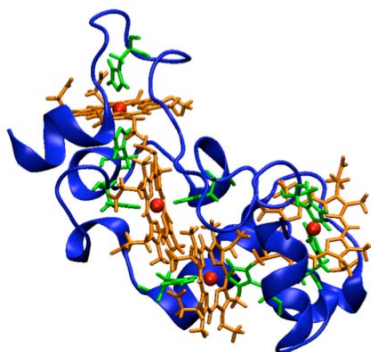


Molecular-Pore Scale Research

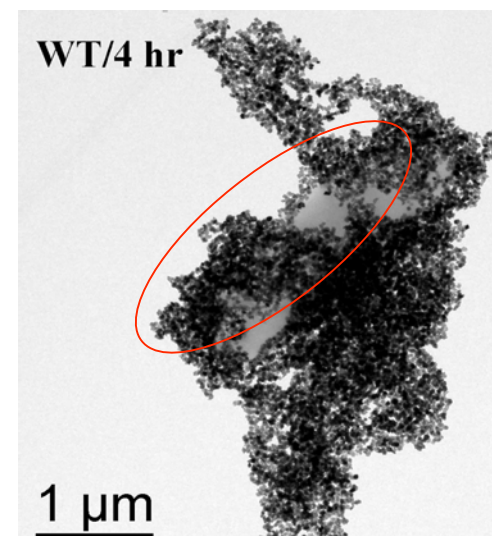
Identify & characterize
reactive molecules

In vitro
kinetic behavior

Interfacial properties
& *in vivo* reactivity



Homogeneous
electron transfer to
Fe(III)-NTA



MRB w/ hematite
nanoparticles

William R. Wiley

EMSL

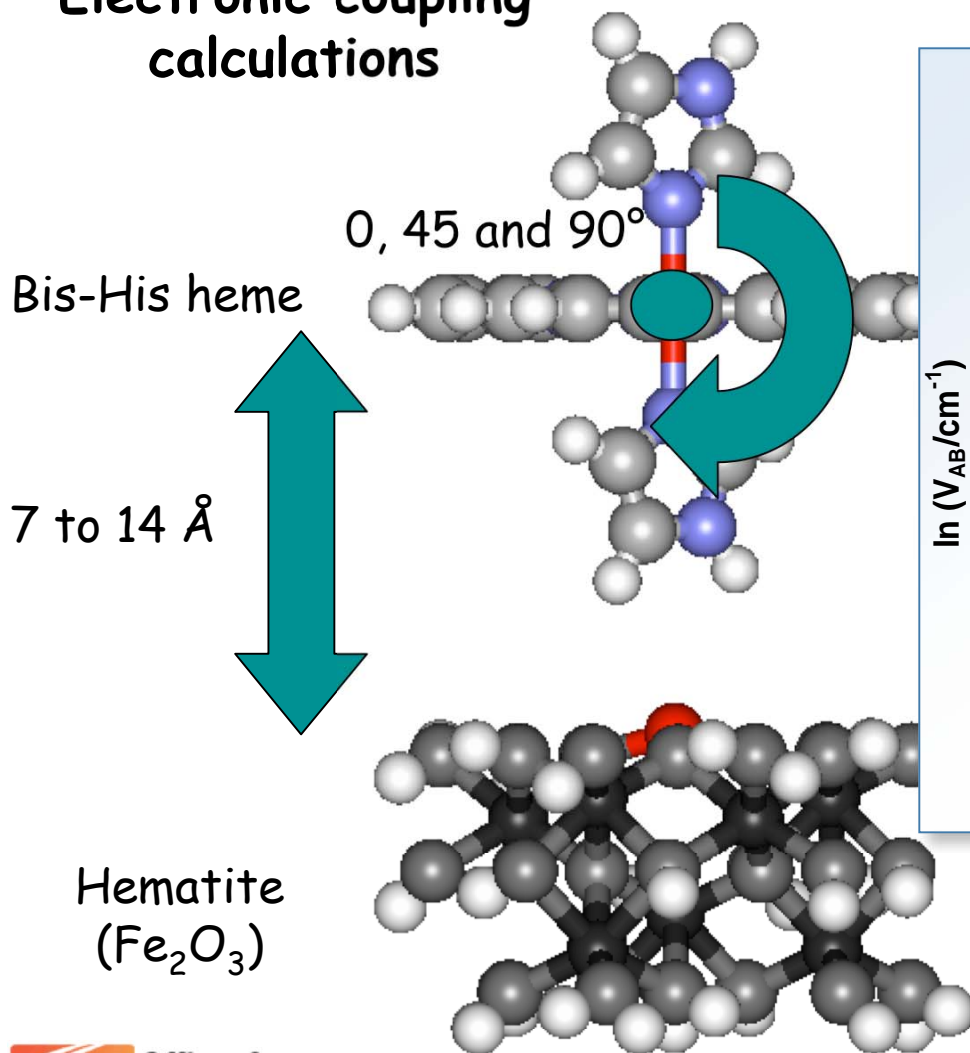
Environmental Molecular Sciences Laboratory

Pacific Northwest National Laboratory
U.S. Department of Energy

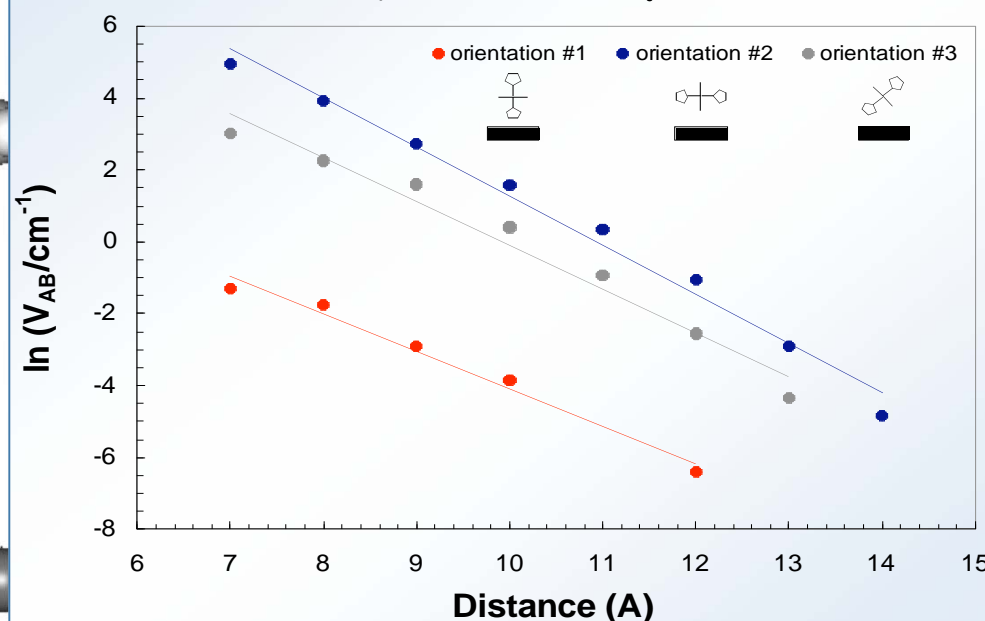
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Orientation/Distance Effects on Electron Transfer Rates

Electronic coupling calculations



Iron Terminated (001) Hematite Surface



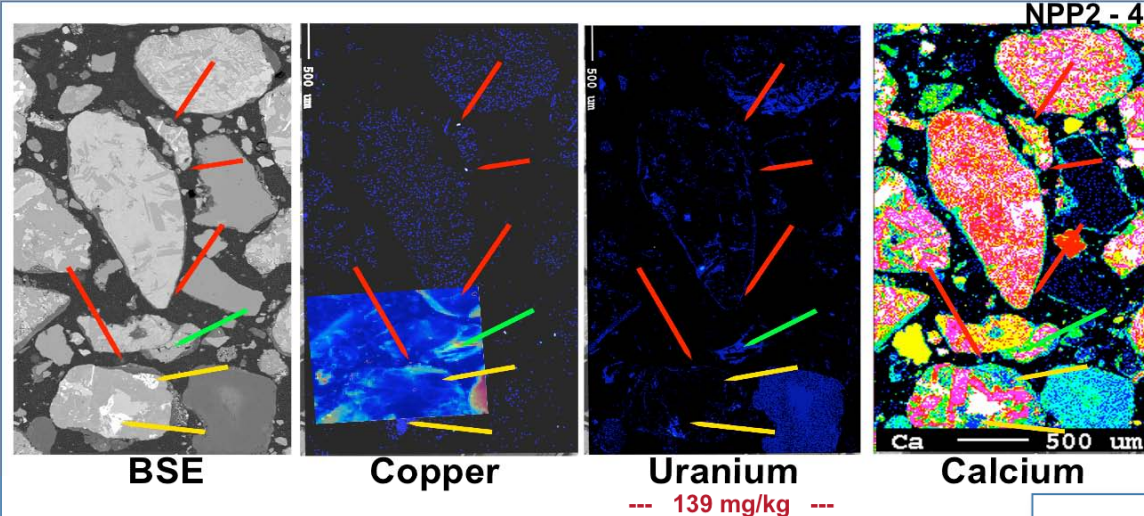
NWChem

Spin unrestricted Hartree-Fock

Fe Ahlrichs VTZ; C,O,N,H 6-31G*

Microscopic Speciation Controls Macroscopic Release Behavior of U

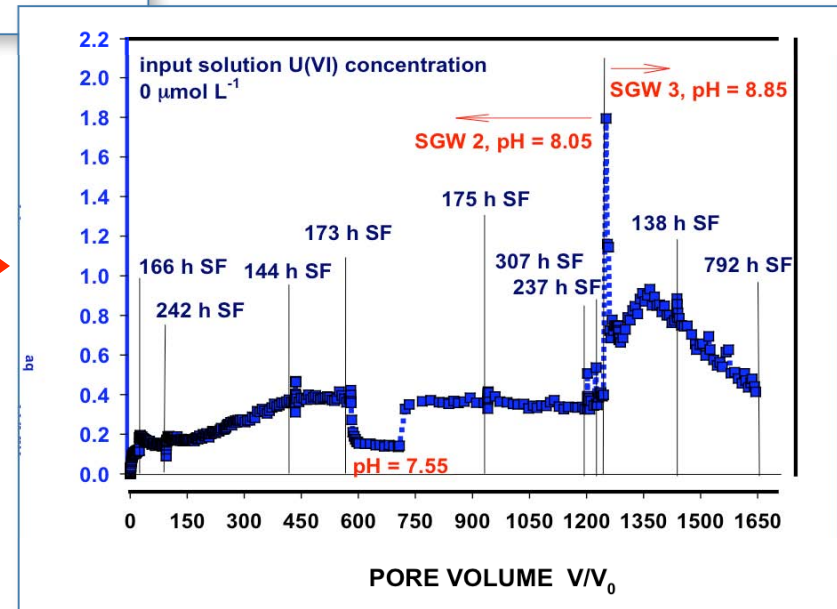
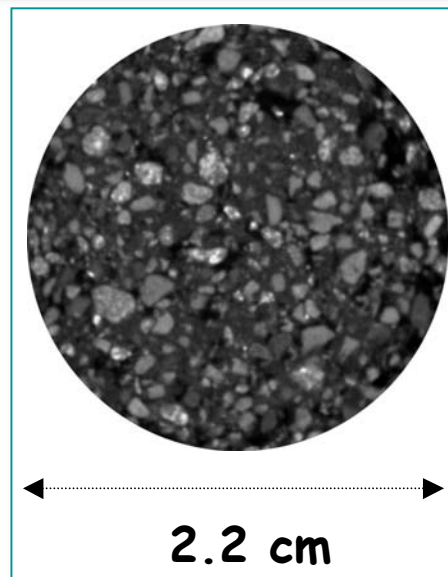
Metatorbernite (uranyl copper phosphate) in grain coatings



- ▶ 300 A sediments contain precipitated U
- ▶ Speciation model developed from EXAFS, S-XRD, and TEM/EPM
- ▶ Column study integrates multiple pore-scale processes

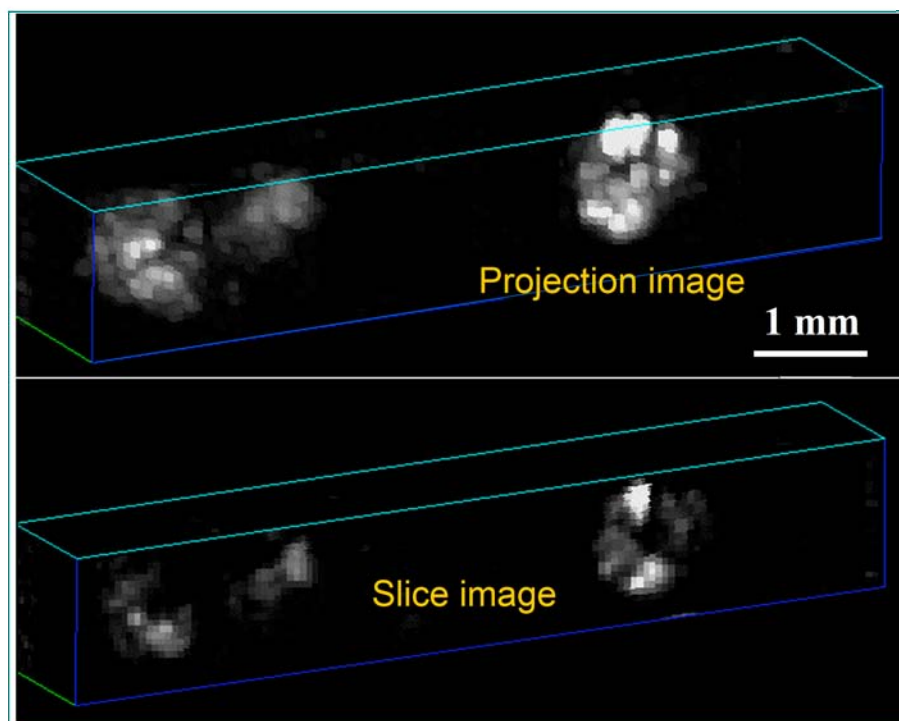
Column study to investigate mass-transfer controlled dissolution

(Catalano et al. 2006, Arai et al. 2007, Zachara et al. 2008)



NMR Pulse Gradient Spin Echo (PGSE) Measurements of H₂O Self-Diffusion in Intragrain Fractures

300 MHz EMSL NMR

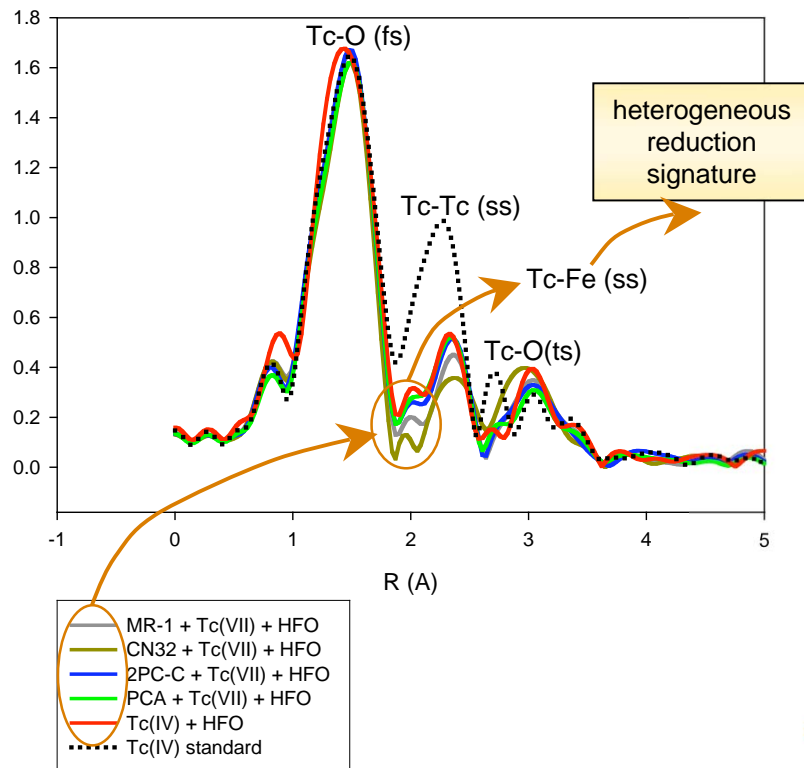


- ▶ Measures magnetic moment under field gradient (G) to determine self diffusion during Δt
- ▶ Determines ensemble of molecular random movements of ¹H-associated with diffusion
- ▶ Data allows calculation of diffusion factors for reactive mineral grains
- ▶ Basis for pore-scale transport models

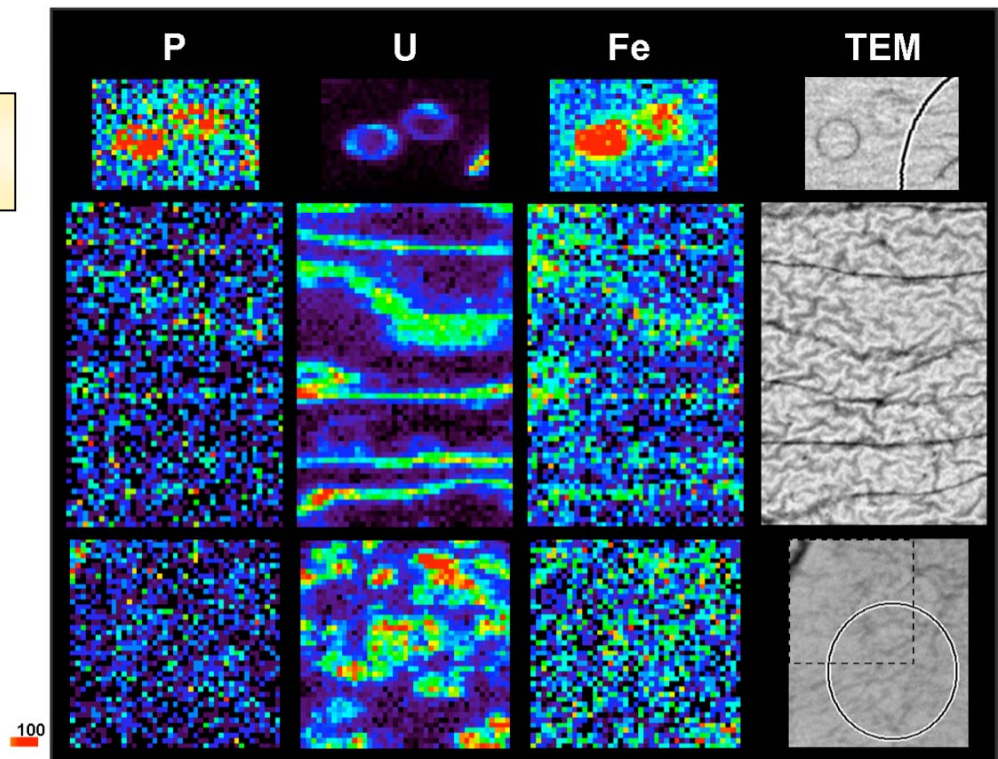
(Liu et al. 2007, WRR)

Synchrotron X-ray Spectroscopy & Microscopy (APS)

Tc EXAFS, S. Heald



X-ray microscopy, Kemner et al.



(Marshall et al. 2006, *PLoS Biology*)

SFA Implementation (FY09-10)

Initial/Transition Science Themes

- ▶ **Microbial ecology investigations of unconfined aquifer in 300A & biogeochemical studies (U and Tc) w/new MRB isolates**
- ▶ **Molecular/microscopic studies of MRB isolates & derived biomolecules in model mineral-water systems**
- ▶ **Molecular speciation & biogeochemical reaction studies of Pu in Z crib sediments and model systems**
- ▶ **Competitive interfacial redox reactions of O₂ and Tc(VII) in Hanford Fe²⁺-containing minerals and 200A deep vadose sediments**
- ▶ **Pore-scale reaction networks, macroscopic transport behavior, and coupled kinetic transport models in 300A sediments**
- ▶ **Geophysical imaging & measurements of different types for facies and transition zone delineation in 300A U plume**